

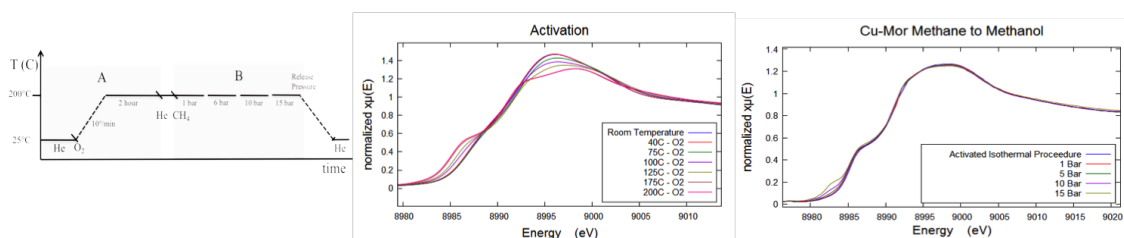
Exploration of activated copper sites for conversion of methane to methanol at low temperature

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Conversion of methane into methanol provides a promising route for harnessing untapped methane resources that are otherwise discarded or flared into the atmosphere. Due to the tendency for methane to fully oxidize, the scientifically challenging part is to only partially oxidize the methane¹. With the combination of the appropriate micropore environment and an exchanged cation, Cu-mordenite and Cu-ZSM-5 can achieve selective methane activation.

Copper in the form of di- or tri cores has been reported as an active species in the conversion of methane to methanol, but requires high temperature activation, typically at 450°C in an oxygen environment. This high temperature activation step has become a standard step in stepwise conversion of methane to methanol throughout literature^{2,3,4}. Contrarily, when the reaction takes place at high methane pressures, Tomkins et al. have shown that high yield ($56.2 \mu\text{mol}\cdot\text{g}^{-1}$) can be achieved without this high activation temperature⁵. Specifically, methane to methanol conversion can be performed isothermally at low temperatures (200°C). These temperatures are well below the activation temperature of the active sites previously proposed (di- or tri-Cu cores).



This work focuses on using in-situ XAS to elucidate the copper speciation and active site responsible for the conversion of methane to methanol under high pressure, low temperature isothermal conditions for copper exchanged mordenite, zeolite Y, and omega. Preliminary results show that, at pressures higher than 1 bar, copper interacts with methane without the need of activating the sample at 450 C. Even for a zeolite like Cu-Y which generally shows low conversion of methane to methanol, a significant increase in conversion is suggested by the XANES results at pressures at or above 15 bar.

1. R. Horn, R. Schlögl, *Cat. Let.*, 145 (2015) 23
2. M.H. Groothaert, P.J. Smeets, B.F. Sels, P.A. Jacobs, R.A. Schoonheydt, *J. Am. Chem. Soc.* (2005) 127, 1394
3. E.M.C. Alayon, M. Nachtegaal, A. Bodi, M. Ranocchiari, J.A. van Bokhoven, *Phys. Chem. Chem. Phys.*, 17 (2015) 7681.
4. S. Grundner, M. Markovits, G. Li, M. Tromp, E. Pidko, E. Hensen, A. Jentys, M. Sanchez- Sanchez, J. Lercher. *Nat. Commun.* 6 (2015) 7546.
5. Tomkins, P., Mansouri, A., Bozbag, S.E., Krumeich, F., Park, M.B., Alayon, E.M.C., Ranocchiari, M. and van Bokhoven, J.A, *Angewandte Chemie*, 128 (2016), 5557-5561